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Determining thermochemical properties of halogenated metals: On enabling the rapid assessment of agent defeat formulations

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Please answer all sections of the document. You are welcome to use figures and tables to complement or enhance the text. For annual reports, please only describe work for the period of performance (July 1, 2013 - June 30, 2014). For final reports, please describe the comprehensive effort.

Grant/Award #: HDTRA1-11-1-45381

PI Name: Dr. Joseph M. Zaug; **Co-PI:** Dr. Sorin Bastea

Organization/Institution: Lawrence Livermore National Laboratory, Livermore, CA

Project Title: Determining thermochemical properties of halogenated metals: On enabling the rapid assessment of agent defeat formulations

What are the major goals of the project?

List the major goals of the project as stated in the approved application or as approved by the agency. If the application lists milestones/target dates for important activities or phases of the project, identify these dates and show actual completion dates or the percentage of completion. Generally, the goals will not change from one reporting period to the next. However, if the awarding agency approved changes to the goals during the reporting period, list the revised goals and objectives. Also explain any significant changes in approach or methods from the agency approved application or plan.

The objective is to provide speeds of sound and equations of state data of halogenated detonation product materials. The EoS information is incorporated into the Cheetah thermochemical code library to thus enable accurate semi-empirical calculations of detonation condition chemistry and performance. The biocidal efficacy of formulated energetic systems may be determined rapidly *in silico* to guide formulation developments and therefore focus large-scale testing efforts onto the most promising munition deliverables.

During the third year of our project we completed a detailed analysis of the equation of state of Ag₂O. Here the EOS is complicated by the persistence of a mixed crystalline followed by an amorphous phase. This information is required for parameterization of exponential-6 interatomic potential parameters utilized within the Cheetah thermochemical code. Parameterization of MgCl₂ (a year three sample) will be completed this calendar year after the EOS is experimentally determined: beamtime at the LBNL/ALS will be available in July/August 2014. The speeds of sound from fluid state BiI₃ were successfully measured to enable more accurate thermochemical calculations/predictions of detonation products where Bi(IO₃)₃ is formulated with energetic materials. (Note: On October 25th 2013, our DTRA program manager, Su Peiris, reprioritized BCl₃ with BiI₃.) The aim is to deliver –post detonation– high concentrations of iodine. To directly measure GPa pressure speeds of sound from BiI₃ (an optically opaque material) a new high-pressure experimental method –originally developed by our group at LLNL– was implemented. Here we leveraged our existing DOE funding to enable our ability to reach DTRA program objectives. Halfway through our third year the laser system required for sound speed measurements failed. Our thirteen-year old Time-Bandwith Products Jaguar laser was shipped back to Switzerland for repairs: it is due to arrive back at LLNL in July. As a result of this critical equipment failure, we requested and were awarded a no cost extension that expires in November of 2014. The added time will enable us to make measurements on additional materials of interest to our DTRA sponsor e.g., BF₃ and SiF₄.

What was accomplished under these goals?

For this reporting period describe: 1) major activities; 2) specific objectives; 3) significant results, including major findings, developments, or conclusions (both positive and negative); and 4) key outcomes or other achievements. Include a discussion of stated goals not met. As the project progresses, the emphasis in reporting in this section should shift from reporting activities to reporting accomplishments.

Accomplishments/New Findings

Ag₂O

We previously measured pressure dependent Ag₂O X-ray diffraction data up to 37 GPa. Ag₂O undergoes a low pressure second-order phase transition at ~ 1 GPa. At 1.28 GPa the cubic phase to hexagonal phase transition is commensurate with a 5 % volume reduction. At ~ 5 GPa Ag₂O begins a transition to a disordered network material. Upon decompression from 30 GPa to 1.3 GPa the oxide undergoes an amorphous to recrystallization transition (See Fig. 1). The recovered material consists of a mixed-phase system that may slowly convert to the pure cubic phase.

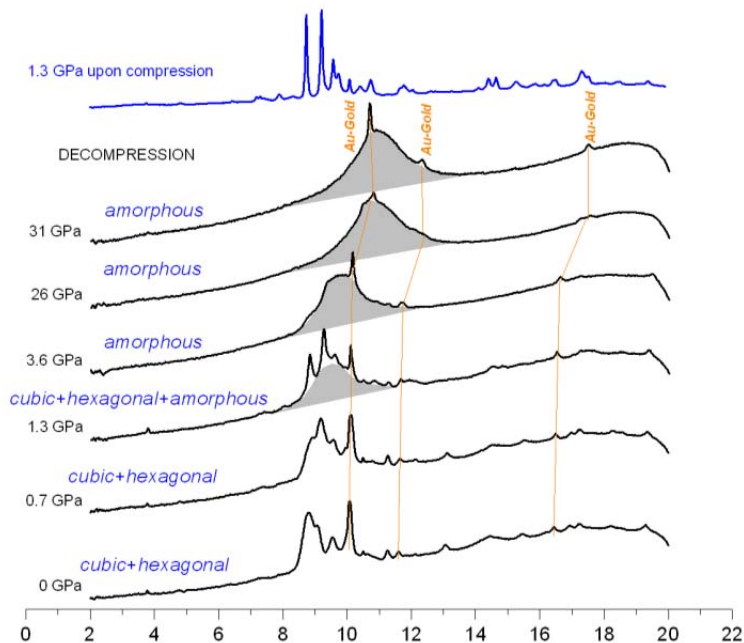


Fig. 1 Selected decompression cycle pressure dependent Ag₂O XRD diffraction patterns. The sequence begins at 31 GPa. The x-axis is in units of 2-theta and the y-axis is in arbitrary units of diffraction intensity. The x-ray energy is 25 keV.

These results partially contradict a Ag₂O EOS paper by Werner et al. where their material remained crystalline up to at least 30 GPa; however, this previous work failed to include ambient condition

materials characterization. Here we report on our efforts to quantify Ag₂O pressure dependent phase fractions including the commensurate phase volumes. The percent phase fraction data are given in Table 1. The phase fractions were determined using phase dependent relative Bragg peak intensity ratios (integrated areas). The refined lattice parameters were used to compute unit cell volumes that are listed in Table 2.

Table 1. Pressure dependent mixed-phase percent fractions of Ag₂O

P (GPa)	Cubic Fraction	Hexagonal Fraction	Amorphous Fraction
0.12	100	0	0
1.3	28	72	0
2.4	24	76	0
4	25	75	0
5	22	76	2
6	18	70	12
7	14	68	18
8	7	46	47
9	5	35	60
11	0	20	80

Table 2. Pressure dependent volume data from cubic and hexagonal Ag₂O

Pressure (GPa)	σ (GPa)	Volume (\AA^3) Cubic Phase	σ (\AA^3)	Volume (\AA^3) Hexagonal Phase	σ (\AA^3)
0.12	0.005	105.862	0.012	-	-
1.30	0.008	103.690	0.056	149.290	0.086
2.40	0.008	103.103	0.055	147.288	0.088
4.00	0.010	101.235	0.066	145.257	0.110
5.00	0.020	100.556	0.067	143.656	0.127
6.00	0.030	100.939	0.095	140.930	0.097
7.00	0.040	100.516	0.077	139.088	0.104
8.00	0.040	99.671	0.121	139.021	0.183
9.00	0.060	97.547	0.163	135.424	0.172
11.00	0.060	95.697	0.055	135.717	0.154
Decompression	-	-	-	-	-
1.30	0.010	102.831	0.122	149.959	0.079
0.70	0.007	102.690	0.083	151.342	0.170
1e-4	0.003	103.162	0.090	156.649	0.100

The ambient pressure-temperature volume for each phase, including the bulk modulus was determined by fitting several EOS models to each phase. The Birch-Murnaghan model (2nd-4th expansion orders), Vinet, and the finite-strain, Ff, models were applied to the cubic phase. For the high pressure

hexagonal phase the Ff model was replaced with the Gg finite strain model. The most optimal fits (reported here) are based on corresponding goodness-of-fit results (see Table 3.). The reported fits were not overly optimal and the principle reason is because there were two and sometimes three mixed phases. Notwithstanding the need to properly index the high pressure phase this is an unusually challenging problem and it may account for the reason why P-V Ag₂O EOS data have never been previously reported.

Table 3. The most optimal (lowest χ^2 value) equation of state model parameters for cubic and hexagonal Ag₂O; **1)** Cubic phase Birch-Murnaghan 2nd order fit, **2)** Cubic phase 1st order Ff model fit; **3)** Hexagonal phase Vinet model fit, **4)** Hexagonal phase Gg model 1st order fit. The corresponding experimental standard deviations are provided for each parameter column. The EOS model parameters are V_0 , the ambient pressure volume, K_0 , the ambient condition bulk modulus, K' the pressure derivative of the bulk modulus, χ^2 , the reduced chi-squared goodness-of-fit value for each least-squares model fit, Max P, the maximum pressure deviation between the model and the data and K-S, the Kolmogorov-Smirnov goodness-of-fit test parameter given here for a Gaussian distribution of data.

	V_0 (Å ³)	esd	K_0 (GPa)	esd	K'	esd	χ^2	Max P	K-S
1 cubic	106.009	0.0232	85.5	5.3	4	-	112.59	2.04	0.495
2 cubic	105.786	0.0232	83.3	8.5	5.61	2.3	86.11	36.82	0.548
3 Hex	151.451	0.2626	90.2	11.3	-0.9	3.6	15.54	1.56	0.436
4 Hex	151.550	1.235	65.835	2.270	4	-	500.8	0.313	0.548

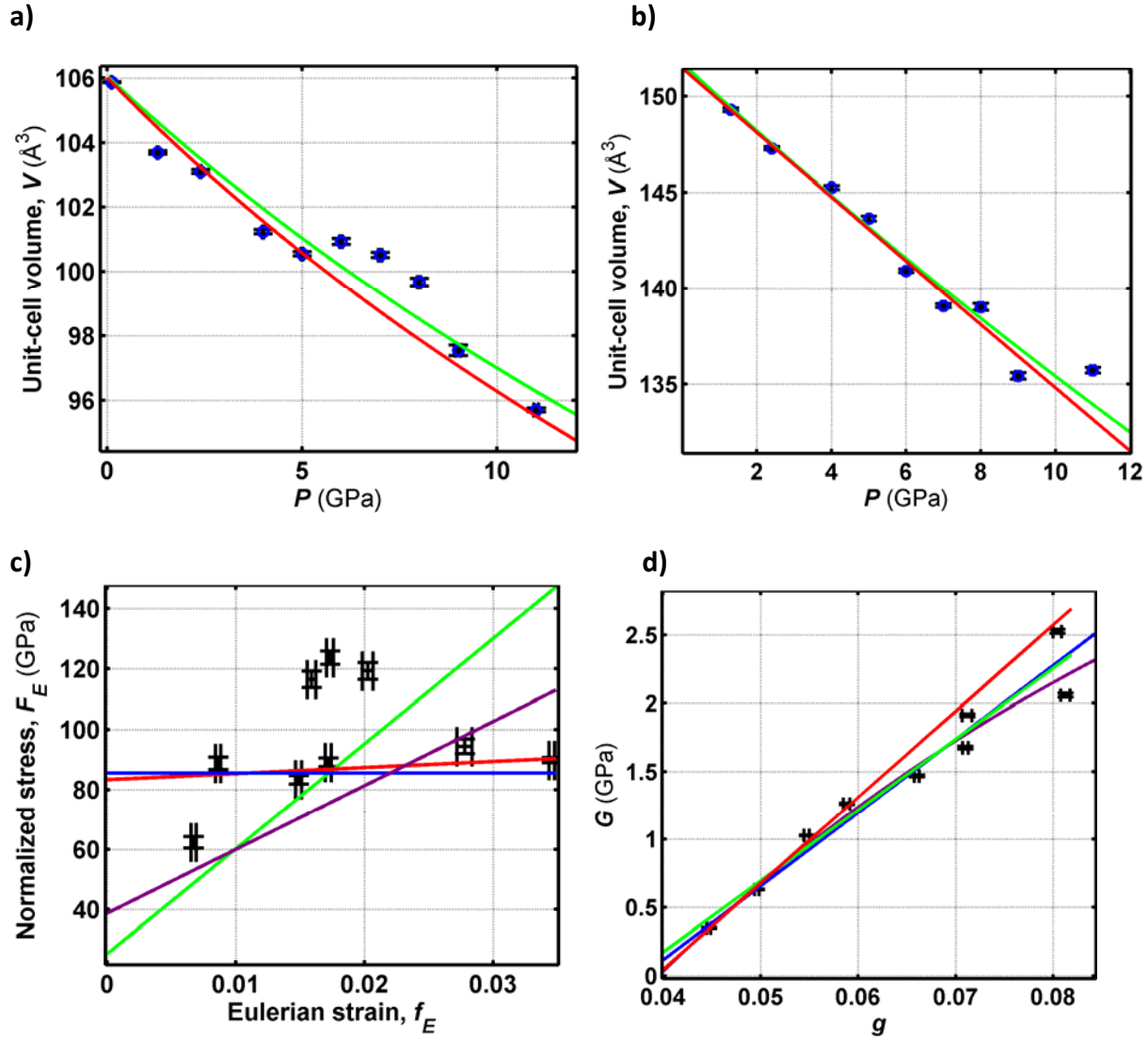


Fig. 2. The most optimal EOS model fits to cubic and hexagonal Ag₂O data. **a)** A second-order Birch-Murnaghan model fit to the cubic phase (red line is a weighted fit and the green line is an unweighted fit); **b)** A Vinet EOS model fit to the hexagonal phase (red line is a weighted fit and the green line is an unweighted fit); **c)** A first-order Ff model fit to the cubic phase (red line is a weighted fit, the green line is an unweighted fit, the blue line is the 2nd-order B-M fit, and the purple line is the Vinet EOS model fit); and **d)** a first-order Gg model fit to the hexagonal phase. The line key in c) also applies to d) where Ff is replaced with Gg.

MgCl₂

Synchrotron Beamtime has recently been allocated at LBNL/ALS to measure the cold-compression curve of MgCl₂ up to 40 GPa. Preliminary experiments will begin in July of 2014. The material (99.99% pure) has been acquired from Sigma-Aldrich chemical company.

BiI₃

To overcome the challenge of directly measuring ultrasonic speeds of sound within the DAC from BiI₃ –an optically dense material- we utilized our new and versatile experimental approach, backreflected photoacoustic light scattering (BRPALS). Here we launch a moderately broadband pulse (10 GHz) at the surface of a diamond culet. The pulse propagates radially along the sample-diamond interface. We then focus a time-delayed probe pulse to backscatter from the travelling pulse and from an ion-etched line in the culet. The geometry and physics of this approach enables the determination of acoustic propagation velocity without knowing the index of refraction from the pressurized material. To determine the effective scattering wavevector, measurements were performed first on pressurized water with well characterized sound speeds.

The first-ever high-pressure sound speed data from BiI₃ are presented in Fig. 3b. The experiment was quite challenging for two reasons: the first is that our laser power and pulse temporal width were markedly degraded due to a failing system (see page one of this report) and the second is because the melting curve of BiI₃ is such that it freezes at less than 0.5 GPa at nearly 800 K. In addition, our diamond-anvil cells are designed to work at many 10's to well above 100 GPa pressures. Nevertheless, our measurements -with higher than normal error bars, were critical to provide a key constraint toward parameterization of the BiI₃ exp-6 interatomic potential values required for accurate and relevant thermochemical calculations.

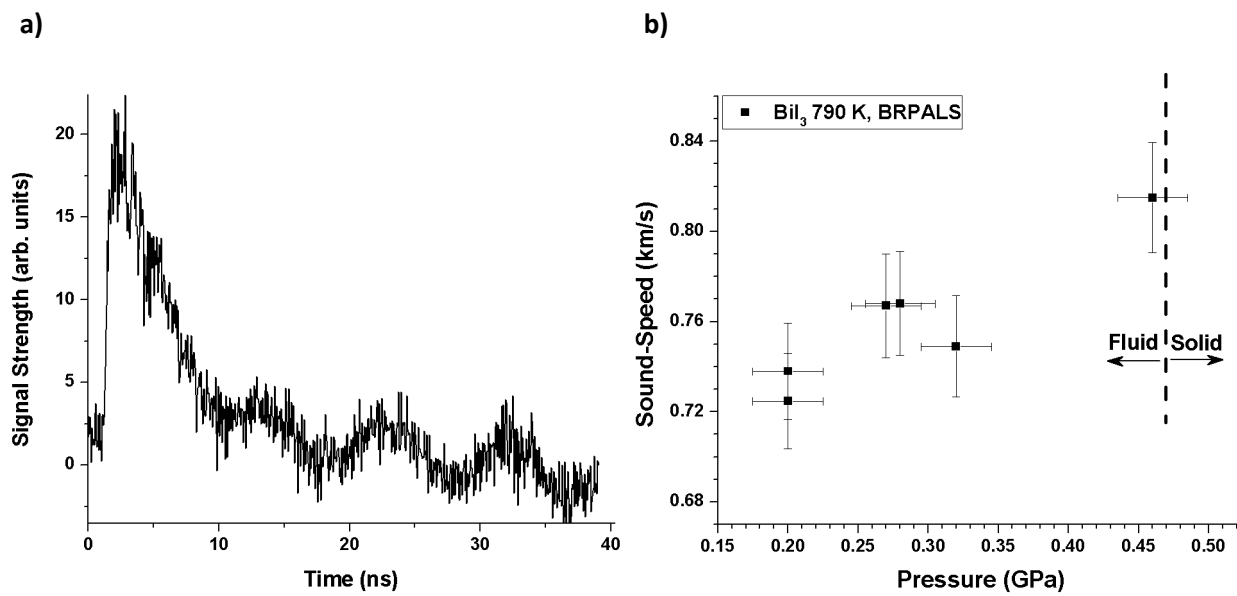


Fig. 3. **a)** Time Domain ultrasonic data from BiI₃ at 0.11 GPa and 790 K. **b)** Pressure dependent sound speed data along the 790 K isotherm.

One goal of this effort is to quantify whether it is feasible to optimize the delivery of iodine using energetic formulations containing $\text{Bi}(\text{IO}_3)_3$. The previous Cheetah version library did not contain Bi as an element for thermochemistry calculations. To remedy this deficit literature data were used to develop a Bi exp-6 interatomic potential: the comparison between our model EOS and the experimental shock Hugoniot data (McQueen and Marsh, 1960) is given in Fig. 4a. The shock Hugoniot of bismuth oxide (Fig. 4b) and the low pressure bismuth phase diagram (Fig. 4c) are also reasonably well-matched by the Cheetah EOS library. Using these EOSs including the new BiI_3 EOS it is now possible to make more confident predictions that are now guiding Cheetah end-users such as James Lightstone and Demitrios Stamatis at NSWC-IH.

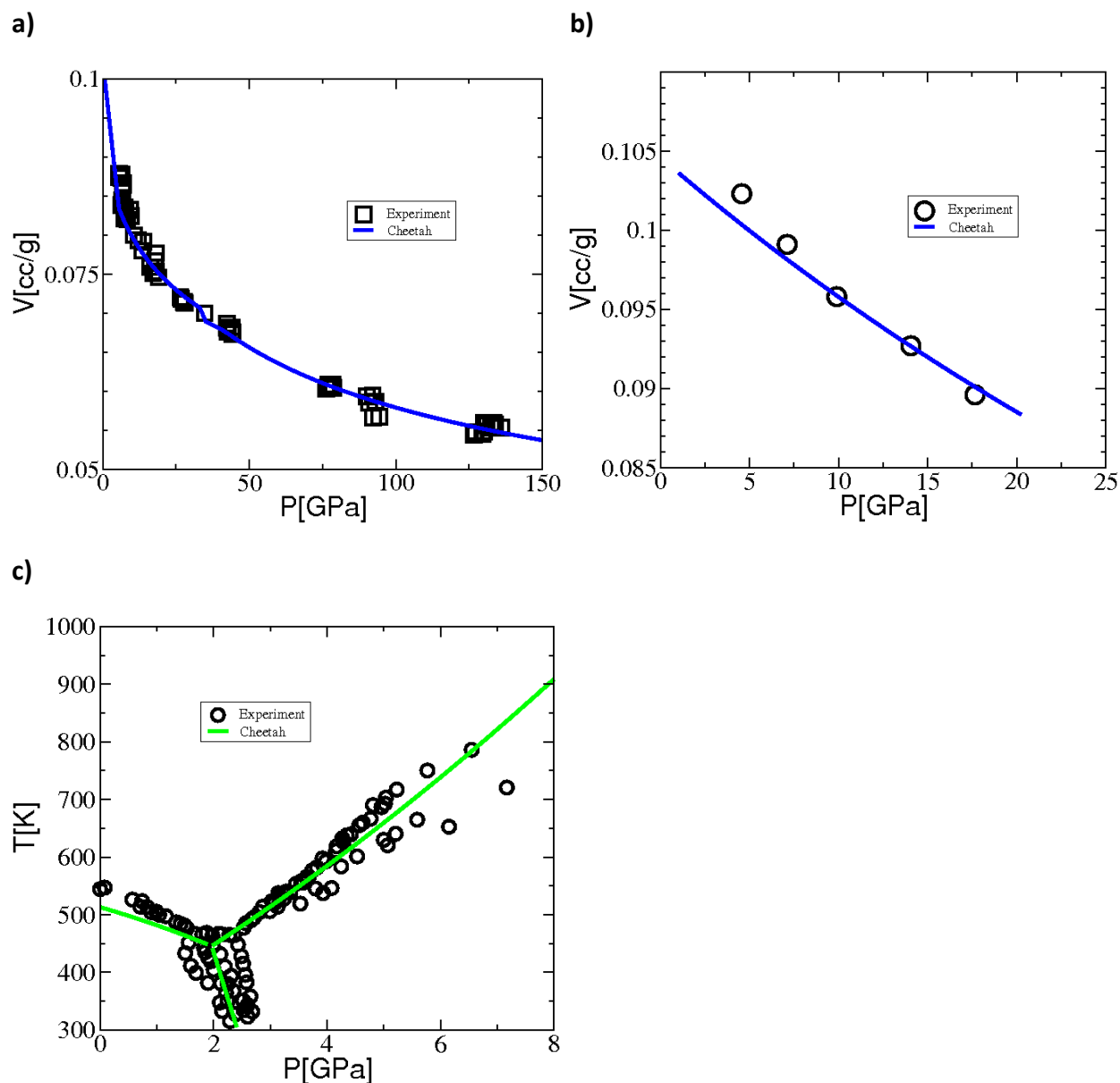


Fig. 4. Comparisons between experiments and the Cheetah EOS library based calculations for a) Bi and b) Bi_2O_3 including c) the low pressure Bi phase diagram.

AlF3 and AlI3

During this third year we have nearly completed (currently at the ~ 98% level of completion) a manuscript communicating our work to determine the EOS of AlF3 and AlI3. This manuscript will most likely be submitted to *PRB* and by no later than August 2014.

References

Werner A. and Hochheimer HD, <i>PRB</i> 25 , 5929, (1982)
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What opportunities for training and professional development has the project provided?

If the research is not intended to provide training and professional development opportunities or there is nothing significant to report during this reporting period, state "Nothing to Report." Describe opportunities for training and professional development provided to anyone who worked on the project or anyone who was involved in the activities supported by the project. "Training" activities are those in which individuals with advanced professional skills and experience assist others in attaining greater proficiency. Training activities may include, for example, courses or one-on-one work with a mentor. "Professional development" activities result in increased knowledge or skill in one's area of expertise and may include workshops, conferences, seminars, study groups, and individual study. Include participation in conferences, workshops, and seminars not listed under major activities.

This project (High Pressure: XRD EOS, Sound Speed EOS, Tabletop Shockwave EOS, and Cheetah Thermochemical Calculations) can be blended with meaningful professional development opportunities; however, during year-three we did not have any students or postdoctoral research associates. We did recruit and offer a postdoctoral position to a highly capable individual, Elissaios Stavrou. Dr. Stavrou may join our group in July 2014. Dr. Stavrou's background is primarily in high-pressure XRD EOS and vibrational spectroscopy.

The opportunities here are meaningful primarily because there are very few research groups in the U.S. who conduct accurate time-domain speed of sound measurements on DAC encapsulated samples. We are also one of two other groups in the U.S. (UIUC and LANL) who currently conduct ultrafast tabletop shockwave measurements. Data from these measurements are critically important to improve the confidence/accuracy of detonation chemistry calculations. Moreover, our team is the only group in the U.S. who has demonstrated the ability to measure sound speeds from optically opaque and/or photosensitive fluids within DACs. These skills and capabilities must be expanded through training opportunities else they may become a lost art. Again, the pressure dependent speed of sound of a material is by far the most rigorous test of the accuracy of interatomic potentials used for thermochemical calculations. The reason is because the sound speed is a derivative property where as for example pressure dependent volume data are only a linear thermodynamic property.

How have the results been disseminated to communities of interest?

If there is nothing significant to report during this reporting period, state "Nothing to Report."

Describe how the results have been disseminated to communities of interest. Include any outreach activities that have been undertaken to reach members of communities who are not usually aware of these research activities, for the purpose of enhancing public understanding and increasing interest in learning and careers in science, technology, and the humanities.

Yes, we are in near constant communication with R&D communities of interest that use the LLNL Cheetah thermochemical code to predict the performance of untested energetic formulations. The work of this project is to build-in an agent defeat toolbox whereby one can calculate concentrations of delivered biocidal and/or chemicidal products. For example, this year we continue to assist personnel at the NSWC-IH who are working to develop formulations to deliver iodine using munitions.

What do you plan to do during the next reporting period to accomplish the goals?

If there are no changes to the agency-approved application or plan for this effort, state "No Change."

Describe briefly what you plan to do during the next reporting period to accomplish the goals and objectives.

With the hopeful addition of Dr. Ellissaios Stavrou (July 2014) to our project we can begin in earnest to convert previous annual reports into journal manuscripts. We can begin to train Dr. Stavrou to conduct sound-speed measurements from high P-T fluids (of high technical value to this DTRA project) such as BF₃ and SiF₄ using the LLNL PALS technique.

If a fourth year of funding is extended we will continue to stand ready to rapidly provide relevant EOS data and thermochemical calculations required to more confidently advance DTRA initiatives.

J.M. Zaug and S. Bastea

LLNL, June 25, 2014

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